Reactive Chemical Transport Simulation to Study Geothermal Production with Mineral Recovery and Silica Scaling

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Abstract. There are vast reserves of dissolved minerals in the hypersaline brines of geothermal fields in the Imperial Valley of California. Recovery of zinc from geothermal brines is being practiced in this area, and recovery of silica, manganese, silver, lead and lithium has been or is being considered. Therefore, the ability to model mineral recovery is very significant in terms of economic development and resource utilization. The reactive geochemical transport simulator TOUGHREACT has been used to model rock-fluid interactions during production from and injection into a hypersaline brine geothermal system. The modeling uses published water chemistry data from Imperial Valley and simplified flow system intended to capture realistic features of the hydrothermal system. A number of simulations were performed using different production/injection rate, pH values and silica concentrations of the injection waters. Results indicate that evolution of temperature and zinc concentration depends on production and injection rate. A lower rate results in a lower temperature drop and higher zinc concentration. A low injection pH significantly enhances the dissolution of sphalerite in the reservoir rock, increasing aqueous zinc concentration. A higher injection silica concentration leads to silica precipitation, but decreases the reservoir porosity only slightly even after 20 years. The purpose of this "numerical experiment" is to gain useful insight into the process mechanisms and conditions and parameters controlling zinc recovery and silica scaling in the reservoir. This example also demonstrates that TOUGHREACT can be a useful tool for simulating these kinds of problems.

Introduction

There are vast reserves of dissolved minerals in the hypersaline brines of geothermal fields in the Imperial Valley of California. Recovery of zinc from geothermal brines is being practiced in this area, and recovery of silica, manganese, silver, lead and lithium has been or is being considered. Geothermal production and mineral extraction from geothermal brines are all affected by reactive chemical processes within the reservoir. Therefore, the ability to model these processes is very significant in terms of economic development and resource utilization. The reactive geochemical transport simulator TOUGHREACT is used to model rock-fluid interactions during production from and injection into a hypersaline brine geothermal system. The modeling uses published water chemistry data from Imperial Valley and simplified flow system intended to capture realistic features of the hydrothermal system. The purpose of this "numerical experiment" is to gain useful insight into the process mechanism and conditions and parameters controlling zinc recovery and its associated silica scaling in the reservoir. It also

demonstrates that TOUGHREACT has the capability to simulate reactive chemical processes in geothermal production and mineral recovery systems.

Pham et al. (2001) present a two-dimensional model for evaluating the reactive chemical transport capabilities of TOUGHREACT for geothermal production modeling. A total of five problems were evaluated, including mineral recovery. In the present study, we use the same two-dimensional model that was used by Pham et al. (2001), but we specify more details on conditions and parameters that control the mineral recovery and its associated silica scaling and perform a number of simulations using different input parameters. These conditions and parameters include production and injection rate, pH, and silica concentration in the injection water. We also use refined mineral kinetic data.

The organization of the paper is as follows. We begin with a description of the reactive geochemical transport simulator TOUGHREACT. Then we describe the setup of the mineral recovery problem. After that, we present simulation results and a discussion that is mainly related to: (1) optimal injecting rate, (2) pH effect, and (3) silica scaling. Finally, we present some conclusions drawn from the simulation study.

Description of the TOUGHREACT simulator

The present study on geothermal production with mineral recovery uses a non-isothermal reactive geochemical transport simulator TOUGHREACT (Xu and Pruess, 1998). This simulator was developed by introducing reactive geochemistry into the framework of the existing multi-phase fluid and heat flow code TOUGH2 (Pruess, 1991). The flow and transport in geologic media are based on space discretization by means of integrated finite differences (Narasimhan and Witherspoon, 1976). An implicit time-weighting scheme is used for the individual components of the model: heat and fluid flow, chemical transport, and geochemical reactions.

TOUGHREACT uses a sequential iteration approach for coupling chemical transport and reaction. After solution of the flow equations, the fluid velocities and phase saturations are used for chemical transport simulation. The chemical transport is solved on a component basis, and the resulting concentrations obtained from the transport are substituted into the chemical reaction model. The system of chemical reaction equations is solved on a grid-block basis by Newton-Raphson iteration, similar to that described in Parkhurst et al. (1980), Reed (1982), and Wolery (1992). The chemical transport and reactions are iteratively solved until convergence.

The simulator can be applied to one-, two-, or three-dimensional porous and fractured media with physical and chemical heterogeneity, and can accommodate any number of chemical species present in liquid, gas and solid phases. A wide range of subsurface thermo-physical-chemical processes is considered. The major processes considered for fluid and heat flow are: (1) fluid flow in both liquid and gas phases under pressure and gravity forces, (2) capillary pressure effect for the liquid phase, and (3) heat flow by conduction, convection and diffusion. Transport of aqueous and gaseous species by advection and molecular diffusion is considered in both liquid and gas phases. Aqueous chemical complexation and gas (CO_2) dissolution and exsolution are considered under the local equilibrium assumption. Mineral dissolution and precipitation can be modeled subject to either local equilibrium or kinetic conditions.

The following processes are neglected in the current version of TOGHREACT: (1) compaction and thermal mechanics, such as micro-fracturing by thermal stress and hydro-fracturing by thermal expansion of pore fluid; (2) the effect of chemical concentration changes

on fluid thermophysical properties such as density and viscosity which are otherwise primarily dependent on pressure and temperature; and (3) the enthalpy of chemical reactions.

Problem setup

In the present study, we adopt a two-dimensional model used by Pham et al. (2001) for evaluating the applicability of TOUGHREACT to geothermal systems. Based on the previous work, we focus our attention on mineral recovery and its associated silica scaling problem. We use the same hydrological and thermophysical parameters that were used by Pham et al. (2001), but refine some chemical parameters such as kinetic rate constants. As shown in Figure 1, the model consists of 50 cubic grid blocks with a constant spacing of 100 m and a total of three wells, one for production, one for injection, and one for observation. Temperature and pressure distributions are maintained by one natural recharge source and one discharge sink. One recharge grid block and one discharge grid block both with infinite volume are connected to the domain for constant pressure and temperature boundaries: 140 bar and 260 ^{o}C for the recharge block and 120 bar and 50 ^{o}C for the discharge block. The temperature and pressure conditions of the recharge and discharge fluid are intended to represent, in a simplified way, the initial-state thermodynamic conditions encountered in the hyper-saline fields in the Imperial Valley of California. The model was first run under natural conditions for 50,000 years to reach a steady-state for fluid and heat flow, and the resulting state-state temperature distribution is presented in Figure 2. Then we simulate reactive chemical transport and fluid-rock interactions using the steady-state as the initial condition. The non-isothermal fluid flow and reactive geochemical transport was simulated for 100 years with injection and production.

The initial chemical composition (Table 1) used for the simulation is based on data reported by Williams and Mckibben (1989). The measured pH value is not available, so we assume an initial pH of 6. During the simulation pH is determined by the chemical reaction system especially sphalerite (ZnS) dissolution and precipitation. Sphalerite dissolution can be schematically written as, $ZnS + H^{+} = Zn^{2+} + HS^{-}$, which may be affected by the presence of other original and altered minerals such as kaolinite, montmorillonite, and illite through their buffering of pH. The reservoir rock in the simulation was assumed to contain only quartz (99% by rock volume), and sphalerite (1%). A more comprehensive representation of mineralogy will be addressed in the future. Mineral dissolution and precipitation is considered to be kinetically controlled, and a first order kinetic rate law was used. We used a rate constant of 1.2589×10^{-14} mol m^{-2}s^{-1} for quartz (Tester et al., 1994). As the rate constant for sphalerite (ZnS) is not available from literature, we assume a value of 1×10^{-11} mol m^{-2}s^{-1}, which is in the same order as the pyrite (FeS$_2$) rate constant 4×10^{-11} mol m^{-2}s^{-1}(Ague and Brimhall, 1989). This sphalerite constant is different from the previous value of 1×10^{-13} mol m^{-2}s^{-1} used by Pham et al. (2001). The initial surface area of each mineral is calculated from its volume fraction multiplied by a total surface area of 1 m^2/dm^3: 0.99 for quartz and 0.01 for sphalerite. Thermodynamic data used were taken from the EQ3/6 V7.2b database (Wolery, 1992).

A number of simulations were performed using different injection rate, different pH and silica concentration in the injection water. We first used a brine production rate of 8 kg/s. This same amount of brine was then injected back into the reservoir assuming that the zinc in the produced fluid has been fully extracted at the surface. Temperature of the injected fluid was assumed to be 75 °C. To select a optimal production rate in terms of energy and mineral (Zn) recovery, we then instead used a larger production/injection rate of 40 kg/s. Considering the

dissolution reaction of sphalerite, it is hypothesized that a lower injection pH may enhance the sphalerite dissolution. To learn the pH effect on zinc recovery, we used three different pH values for injection water: 6, 4 and 2. To examine silica scaling and porosity change, the final simulation artificially uses a silica concentration 4 times large than given in Table 1.

Results and discussion

Injection rate

The intermediate pH value of 4 was used in the two production/injection rate simulations. Evolution of temperature and zinc concentration at observation and production wells obtained with the two flow rates is presented in Figures 3 and 4, respectively. A rate of 8 kg/s results in a slight 20-year temperature drop at the production well (216 to 201 ^{o}C), with nearly stable temperature thereafter (Figure 3a). In contrast, a 40 kg/s rate causes a significant 20-year temperature drop to about 140 ^{o}C at the production well, and a small decline thereafter (Figure 3b). For the lower injection rate, zinc concentration at the production well (Figure 4a) is about 2×10^{-6} mol/kg until 20 years. Then, zinc concentration increase to close to 3.5×10^{-6} mol/kg after 100 years. For the higher rate, zinc concentration at the production well (Figure 4b) reaches rapidly a peak value of about 3.5×10^{-6} mol/kg (after about 6 year), because injection waters arrive at the production well faster. Then, zinc concentration decrease to a stable value of 1.6×10^{-6} mol/kg. The temperature drop depends on reservoir dimension and thermophysical conditions and parameters. The zinc concentration depends on not only the same physical conditions and parameters, but also on chemical conditions and parameters such as thermodynamic and kinetic rate constants. Both physical and chemical conditions and parameters are to some degree uncertain. However, as a numerical experiment the results reflect a general trend and give us a preliminary understanding of the evolution of temperature and chemical concentration. In addition, the location, distance, number of injection and production wells all affect the evolution. These issues should be addressed in the future. For the objective of optimizing both energy and mineral recovery using pH adjustment, we then selected the lower injection rate of 8 kg/s for the following simulations.

Effect of injection pH

In addition to the zinc concentration from an injection pH of 4 as shown in Figure 4, we now present zinc concentration evolution obtained using a higher pH of 6 and a lower pH of 2 (Figure 5). With injection at pH 6, the concentration at the observation well decreases to essentially zero after 15 years. This is because sphalerite does not dissolve between the injection and observation wells at this high pH (as well as low temperature at this region) and the zero zinc concentration injection water eventually displaces the reservoir water. The concentration at the production well, which receives a mixture of cold injection water and hot recharge water which continue to dissolve sphalerite, gradually decreases to a stable concentration of 1.4×10^{-6} mol/kg.

With injection at pH 2, the concentration at the observation well reaches as high as 5×10^{-4} mol/kg, and the concentration at the production well reaches 5×10^{-6} mol/kg. Both concentrations are higher than those obtained with the high values of pH (Table 2). A significant concentration difference between observation and production wells can be found for an injection pH of 2. This suggests that sphalerite precipitation occurs between the two wells, which is

confirmed by Figure 6: precipitation does occur in the area surrounding the production well. From Figure 6, we also see that major dissolution occurs surrounding the injection well and minor dissolution occurs just downstream from the observation well, due to the favorable combination of temperature and pH. These results indicate that a low pH enhances dissolution of sphalerite, but an extremely low pH such as 2 causes considerable precipitation of sphalerite before injection water arrives at the production well. Among the three pH values used, an intermediate value of 4 may be the most effective and efficient. The aqueous zinc concentration obtained with this injection pH of 4 is presented in Figure 7, but it should be pointed out that the possible precipitation depends on many factors including both the well distance and chemical kinetics.

Silica scaling

Silica scaling and possible reservoir damage from the silica precipitation have been a major concern for geothermal production. We use the simulation with an intermediate injection pH of 4 to illustrate the problem of silica scaling and porosity change. With an injection silica concentration of 9.02×10^{-3} mol/kg as listed in Table 1, quartz (a silica mineral) precipitation occurs at the injection region due to decreased temperature and solubility (Figure 8). Some quartz also precipitates at the upstream side of the production well because the upwelling water from the recharge area has a higher temperature and contains a higher silica concentration. The overall change in porosity due to precipitation and dissolution of both quartz and sphalerite is very small even after 20 years (below 0.1%, see Figure 9). To enhance the silica precipitation, we artificially increased the injection silica concentration by four times to 3.608×10^{-2} mol/kg, which may provide a upper limit for the silica scaling problem, yet a after 20 years, a maximum porosity change of only 0.3 % can be observed close to the injection well (Figure 10). This indicates that silica scaling in the geothermal reservoir may not be significant. We should point out that in the present simulation, the coarse grid and homogeneous medium used both may underestimate the extent of silica scaling in some localized areas.

Conclusions

We have performed a number of simulations for the 2-D problem of geothermal production with mineral recovery using the reactive geochemical transport simulator TOUGHREACT. Results indicate that evolution of temperature and zinc concentration depends on injection and production rate. A lower rate of 8 kg/s results in a lower temperature drop and higher zinc concentration (an optimal energy and mineral recovery). A low pH enhances dissolution of sphalerite and obtains a higher zinc concentration at the production well, but an extremely low pH such as 2 causes considerable precipitation of sphalerite before injection water arrives at the production well. Among the three pH values used, an intermediate value of 4 may be effective and efficient. For this homogeneous medium, a higher injection silica concentration leads to silica precipitation, but decreases the reservoir porosity only slightly for a limited time span (20 years).

The present simulation results are specific to the reservoir conditions and parameters considered, and water and mineral compositions used in this study. Because of numerous uncertainties such as the chemical kinetics and the lack of sufficiently detailed characterization data at field sites, care should be taken when extrapolating the results and conclusions. Our "numerical experiments" give a detailed view of the dynamic interplay between coupled

thermalphysical and chemical processes, and useful insight into process mechanisms and conditions and parameters controlling zinc recovery from the reservoir. This example also demonstrates that TOUGHREACT could be a useful tool for simulating geothermal production with mineral recovery.

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**Table 1.** List of aqueous chemical concentration.

Chemical	Na^+	Ca^{+2}	K^+	Cl^-	$SiO_2(aq)$	inorganic C as CO_2
ppm-wt	53000	28800	24600	155000	400	500
mol/kg H_2O	3.123	0.973	0.852	5.92	0.00902	0.0154

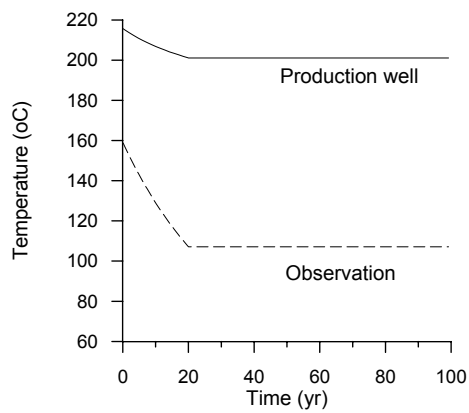**Table 2.** Concentrations (mol/kg H_2O) at observation and production wells after 20 years of production.

pH	Observation	Production
2	9×10^{-4}	5×10^{-6}
4	9×10^{-6}	3.5×10^{-6}
6	0.0	1.4×10^{-6}
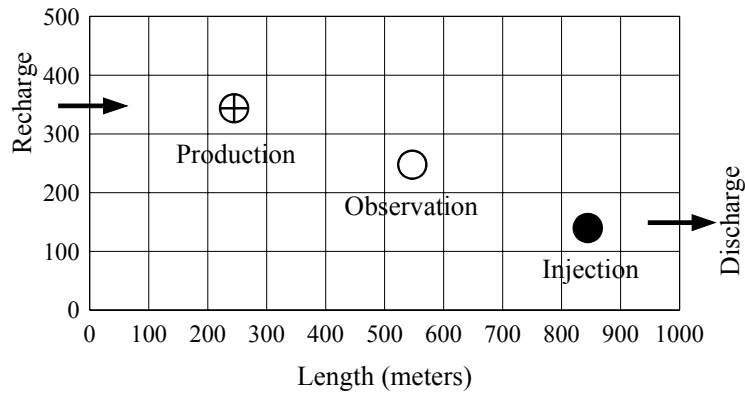
Figure 1. Overview of the two-dimensional model used for simulation of geothermal production with mineral recovery.
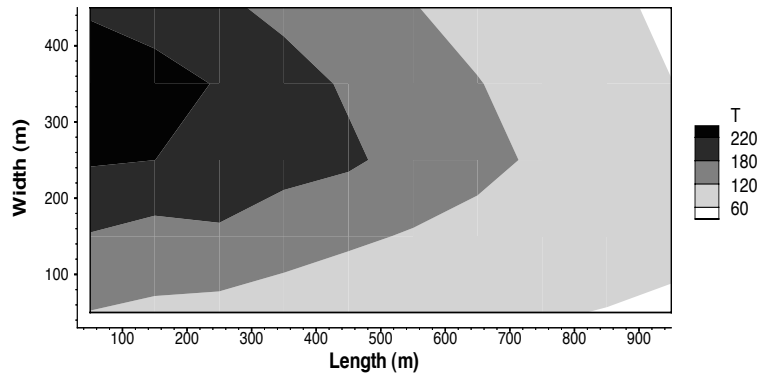
Figure 2. Initial (natural background) temperature (^{o}C) distribution.
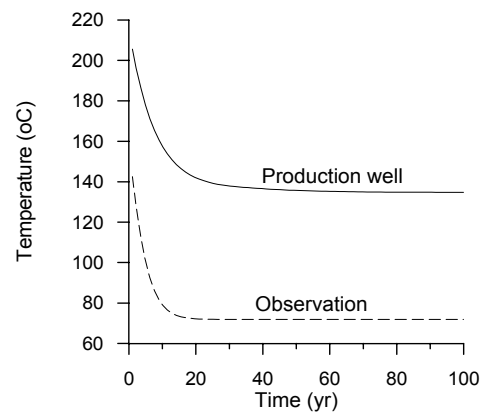
| (a) 8 kg/s | (b) 40 kg/s |

Figure 3. Temperature evolution at observation and production wells obtained with two different injection rates.
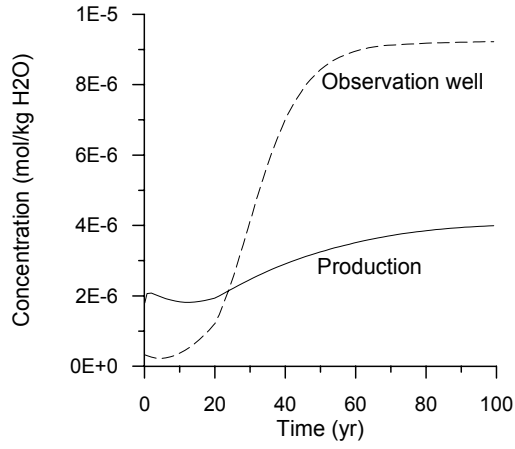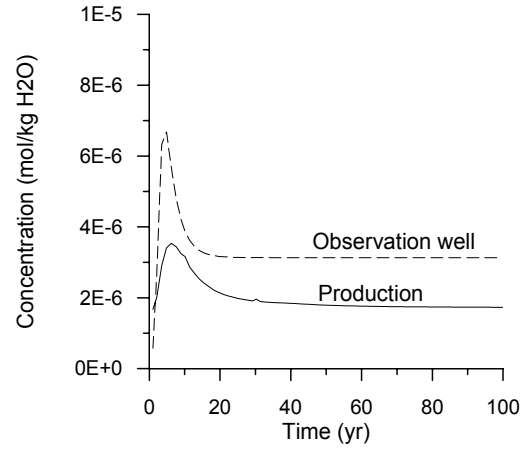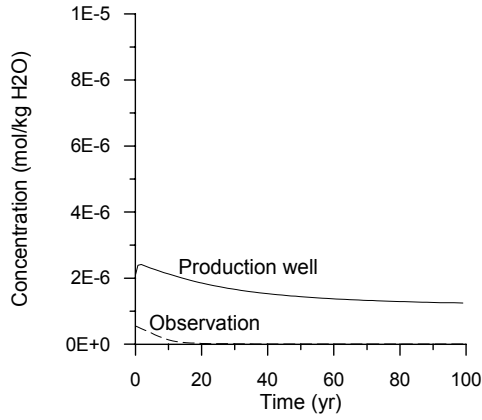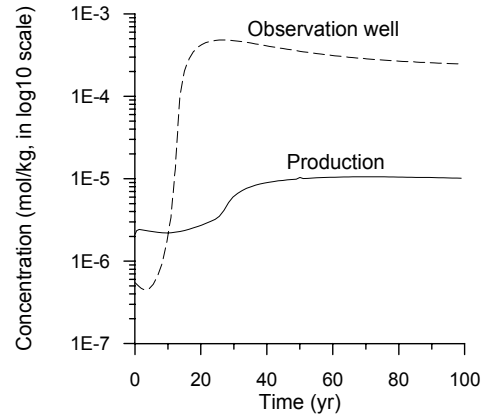
(a) 8 kg/s   (b) 40 kg/s

Figure 4. Evolution of aqueous zinc concentration at observation and production wells obtained with two different injection rates (using an injection pH of 4) .
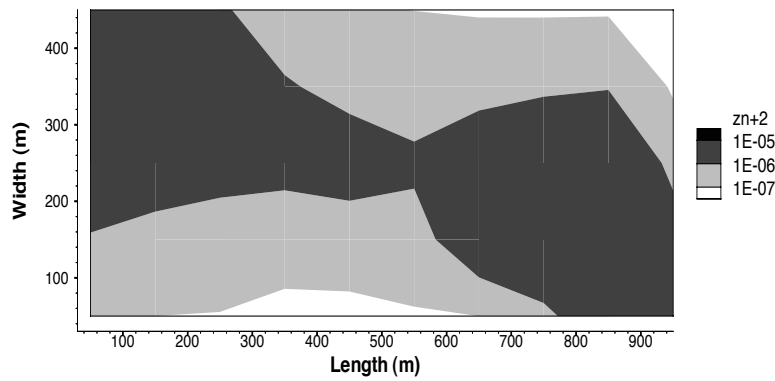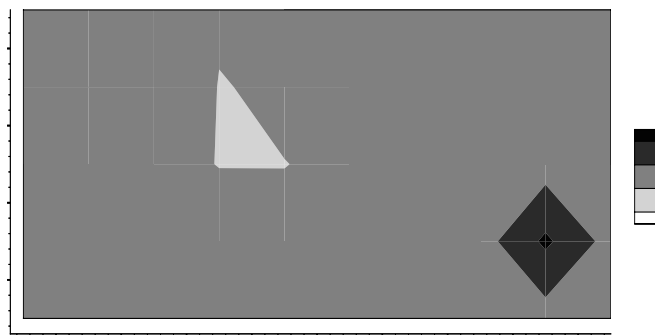

(a) pH = 6   (b) pH = 2

Figure 5. Evolution of aqueous zinc concentration at observation and production obtained using a higher injection pH of 6 and a lower of 2 .
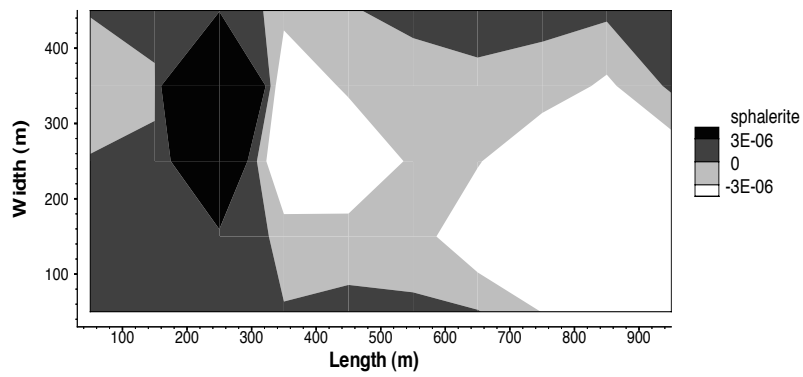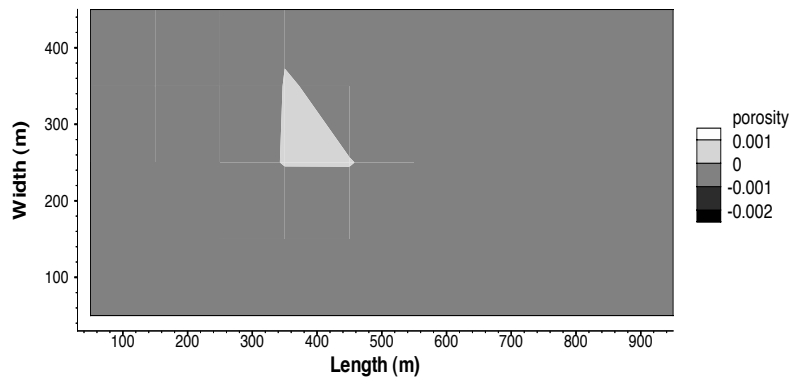
Figure 6. Change of abundance of sphalerite (in volume fraction) after 100 years obtained using an injection pH of 2.
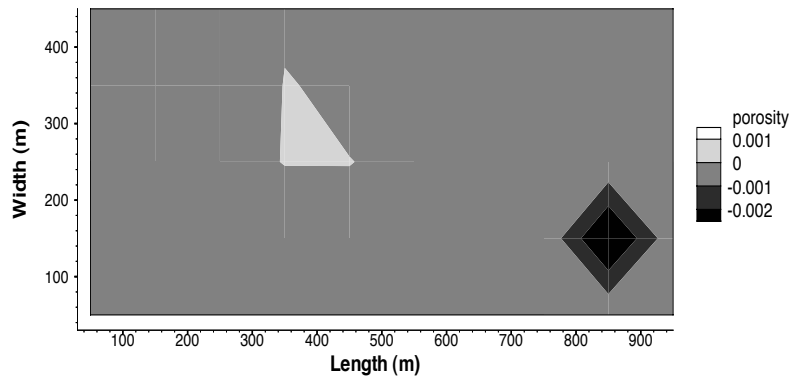

Figure 7. Aqueous zinc concentration after 20 years obtained using an injection pH of 4.

Figure 8. Change of abundance of quartz (in volume fraction) after 20 years obtained using an injection pH of 4.

Figure 9. Change of porosity after 20 years obtained using a pH of 4.

Figure 10. Change of porosity after 20 years obtained using a four times high silica concentration in injecting water (using an injection pH of 4).